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Pearson type VII as a profile shape function and optimization of adjustable parameter *m* with the aid of *R*(*x*) test

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Abstract : Pearson type VII *i e* $Y = Y_0\left(1 + X^2/ma^2\right)^{-m}$ is widely used as a profile fitting function for the purpose of fitting observed peaks in an X-ray or powder neutron diffractogram, particularly in the field of Rietveld studies In order to fit an experimentally observed peak with Pearson type VII, one needs the optimum value of m for which the said profile shape function fits best Pearson type VII is a broad spectrum analytical function, its shape changes from pure Lorentzian with $m = 1$ to pure Gaussian with $m = \infty$, through intermediate Lorentzian, modified Lorentzian and variable Lorentzian with $m = 1.5$, $m = 2$ and $m = 2 - \infty$, respectively. Present author proposes a method for optimizing Pearson type VII with the help of $R(x)$ test [1,2] and tested its efficiency with experimentally observed data from 40% copper-nickel alloy

Keywords : Profile shape function, Pearson type VII, Rietveld method

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Rietveld method [3,4] of structural study is based upon the assumption that all peaks in an X-ray or neutron powder diffractogram could be fitted to a single type of analytical functions like Gaussian, Lorentzian or Intermediate Lorentzian *etc*. The present authors questioned its validity time and again [1,2,5–7]. A probe, *viz* $R(x)$ test was introduced [1,2,7] to investigate and ascertain the nature of all the peaks in a diffractogram and the methodology is described in detail elsewhere [7]. However, in the above mentioned works, Pearson type VII was not taken into account.

Present work not only applied $R(x)$ test to Pearson type VII function, but also finds a simple method of optimizing m with the aid of $R(x)$ test.

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The method involves drawing of an experimentally observed $R(x)$ *versus* x curve, followed by matching the theoretical values of $R(x)$ at $x = m^{1/2} \cdot a$ (where $2a$ is the full width at half maximum intensity for all practical purposes) for different integral and half integral values of m with the experimental values of $R(x)$ at $x = m^{1/2}.a$ for different values of m, except $m = \frac{1}{2}$. From the best match among these two values, optimum m could be ascertained to the nearest integral or half integral values (except $\frac{1}{2}$). Once the best match is obtained, m could be further optimized using numerical technique to other fractional values.

Mitra [1,2] showed that two functions $R(x)$ and $Q(x)$ may yield nearly identical numerical values over a large range of x so that fitting either function with experimentally observed curve is often enigmatic. To overcome this problem Mitra innovated the $R(x)$ test where,

$$R(x) = \int_0^x F(x)dx \quad \text{or} \quad \int_0^x Q(x)dx$$

and showed that fitting the experimentally observed $R(x)$ *vs* x with the theoretically drawn $R(x)$ *vs* x curve is unique and non-ambiguous.

In this particular case, the function in question is Pearson type VII, given by

$$Y = Y_0 \left| 1 + \frac{\quad}{ma^2} \right.$$

where Y_0 is the peak height and could be equated with unity without disturbing the shape of the curve. For $Y_0 = 1$, the function Y could be multiplied by the peak height of the experimentally observed peak to achieve the desired fit, and a is a constant which could be considered equal to $\frac{1}{2}$ (FWHM) of the experimentally observed peak for all practical purposes.

$$Y = \left| 1 + \frac{\quad}{ma^2} \right| \tag{1}$$

Hence, $$R(x) = \int_0^x Y dx = \int_0^x \left(1 + \frac{x^2}{ma^2} \right) dx. \tag{2}$$

Putting $$\frac{\quad}{m^{1/2}.a} = z,$$

we get $$R(x) = m^{1/2}.a \int_0^{z} \left(1 + z^2\right)^{-m} dz. \tag{3}$$

Now putting $z = \tan\theta$, we have

$$R(x) = m^{1/2}.a \int_0^{\theta} \cos^{(2m-2)}\theta \cdot d\theta. \tag{4}$$

This integral can be easily evaluated with m = 1, 1.5, 2, 2.5 *etc*. upto 6 or 7, because Pearson type VII converges to Gaussian at x = 6 or 7. Hence, theoretical $R(x)$ for all possible m with integral and half integral values, could be drawn for comparison with the experimental $R(x)$.

Now the question arises for which m value, the experimental curve fits best with the theoretical Pearson type VII. One method is to draw $R(x)$ *vs* x curves for all possible m and to compare them with experimental $R(x)$ *vs* x curve, which is labourious.

The other way out is to solve for m from the eqns. (5) and (5a) given below [8].

Let $2m - 2 = 2p$ or $2p + 1$.

(i) For $2m - 2 = 2p$,

$$R(x) = \int_0^{\theta} \cos^{2p} d\theta = \frac{1}{2^{2p}} \binom{2p}{p} x + \frac{1}{2^{2p-1}} \sum_{k=0}^{p-1} \binom{2p}{k} \frac{\sin(2p-2k)x}{2p-2k}. \quad (5)$$

(ii) For $2m - 2 = 2p + 1$,

$$R(x) = \frac{1}{2^{2p}} \sum_{k=0}^{p} \binom{2p+1}{k} \frac{\sin(2p-2k+1)x}{2p-2k+1}, \quad (5a)$$

which is extremely difficult to workout, if not impossible.

This problem has been tackled in an elegant fashion as follows.

At $z = 1 = \dfrac{x}{m^{1/2}.a}$, integral (4) could be written as

$$R(x) = m^{1/2}.a \int_0^{\pi/2} \cos^p \theta \, d\theta \qquad \text{where } p = 2m - 2.$$

Now this can be compared with the standard Beta function

$$B(M,N) = \int_0^1 x^{M-1}.(1-x)^{N-1}, dx = 2\int_0^{\pi/2} \sin^{(2M-1)} \theta \cdot \cos^{(2N-1)} \theta \, d\theta \quad (6)$$

or

$$\int_0^{\pi/2} \sin^{(2M-1)} \theta \cdot \cos^{(2N-1)} \theta \, d\theta = \frac{1}{2} B(M,N) = \frac{\Gamma(M).\,\Gamma(N)}{2.\Gamma(M+N)} \quad (7)$$

In our case, the integral is

$$\int_0^{\pi/2} \cos^p \theta \, d\theta \qquad \text{where } p = 2m-2.$$

Comparing with (7),

We have $2M - 1 = 0$ and $2N - 1 = p$, hence, $M = \dfrac{1}{2}$, $N = \dfrac{p+1}{2}$.

Therefore, $\quad m^{1/2}.a \int_0^{\pi/2} \cos^p \theta .\, d\theta = m^{1/2}.a.\, \frac{1}{2} B(M,N)$

$$= \frac{1}{2} \frac{\Gamma\left(\frac{1}{2}\right)\cdot \Gamma\left(m-\frac{1}{2}\right)\cdot m^{1/2}\cdot a}{\Gamma(m)} \tag{8}$$

When $z = 1$, $x = m^{1/2}\cdot a$

This identity could be written as

$$R(x)_{\text{at } x = m^{1/2} a} = \frac{\Gamma\left(\frac{1}{2}\right)\cdot \Gamma\left(m-\frac{1}{2}\right)}{\Gamma(m)} .\, m^{1/2} .\, a \tag{9}$$

The best fit of this identity (9) for a chosen 'm' value optimizes 'm'.

In case of 220 reflection of 40% Cu–Ni alloy, (data taken from Mitra and Dasgupta [7], the best fit of experimental $R(x)$ at $x = m^{1/2}.a$ was observed at $m = 2.5$, given $a = 0.81$, for 220 reflection from the identity (9). This was further corroborated by comparing the experimental $R(x)$ with the theoretical $R(x)$ for Pearson type VII with $m = 2.5$ as shown in Figure 1. Now it is evident from Figure 1 that true value of m lies in the vicinity of 2.5.

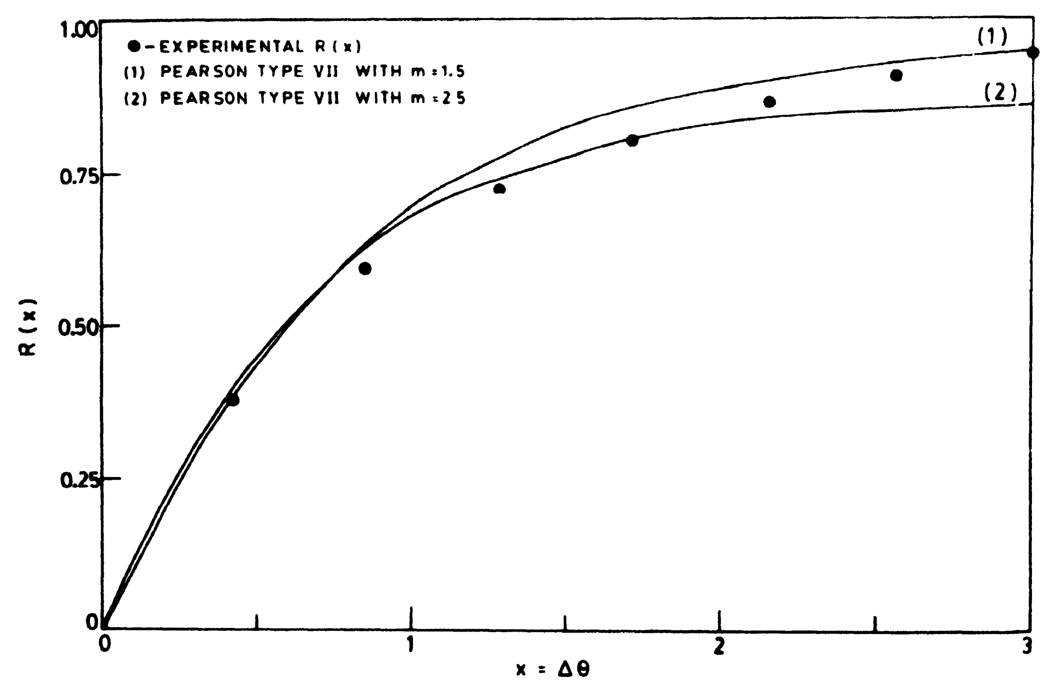

Figure 1. Comparison of experimentally observed $R(x)$ for 220 reflection of 40% Copper-Nickel alloy with the $R(x)$ for Pearson type VII with $m = 1.5$ and 2.5.

Theoretical $R(x)$ *vs* x curves with several fractional m values in the vicinity of 2.5 were drawn using numerical technique (Simpson's $\frac{1}{3}$ rule) and the best fit was acheived at $m = 2.6$ as shown in Figure 2.

The method has one short coming. Optimization method does not work for $m = 0.5$ as the identity (9) is undefined at $m = 0.5$ as $\Gamma(0)$ is undefined.

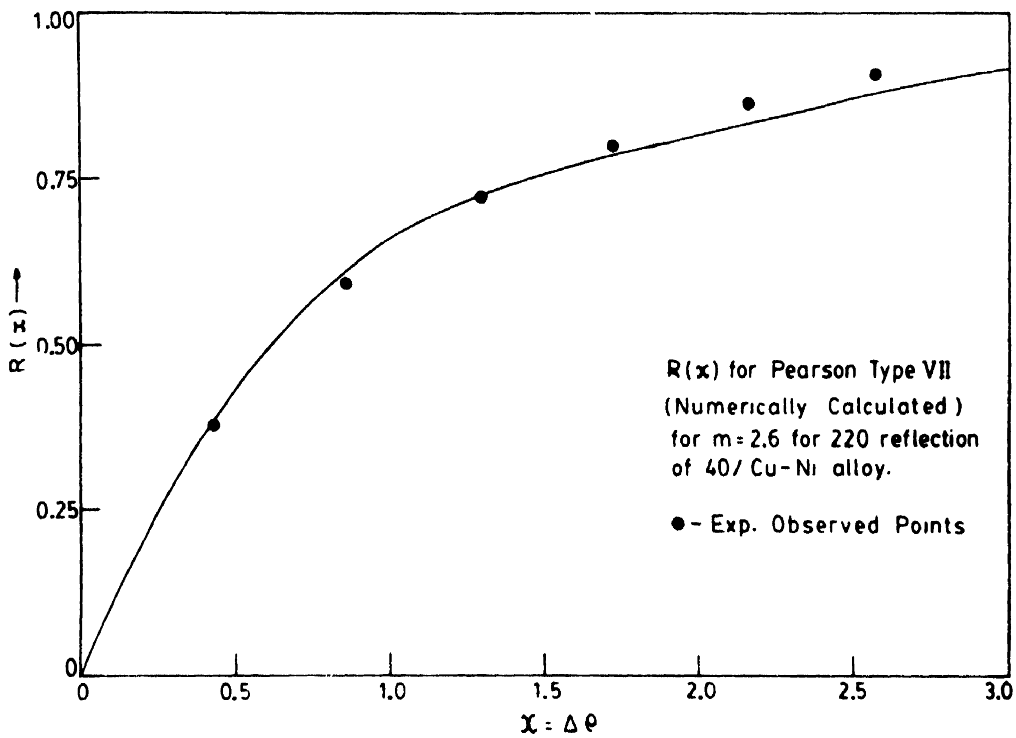

Figure 2. Comparison of experimentally observed $R(x)$ for 220 reflection of 40% Copper–Nickel alloy with numerically calculated $R(x)$ using Pearson type VII with $m = 2.6$

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References

[1] G B Mitra *Acta Cryst* **16** 429 (1963)

[2] G B Mitra *Brit J Appl Phys* **16** 77 (1965)

[3] H M Rietveld *Acta Cryst* **22** 151 (1967)

[4] H M Rietveld *J Appl. Cryst.* **2** 65 (1969)

[5] G B Mitra *Proc Indian Nat. Sci. Acad.* **47A** 47 (1981)

[6] G B Mitra and P Das Gupta *Indian J. Phys.* **61A** 243 (1987)

[7] G B Mitra and P Das Gupta *Indian J Phys.* **69A** 427 (1995)

[8] I S Gradshteyn and I M Ryzhik *Table of Integrals, Series and Products* (New York : Academic) p132 (1980)